Liquid chromatographic analysis of geological organic substances of industrial importance

By

Thelma-Jean Whelan

UNIVERSITY OF TECHNOLOGY SYDNEY

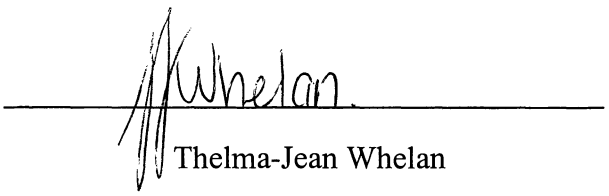
This thesis is submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

2005

CERTIFICATE OF AUTHORSHIP

I herby certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree. I also certify that this thesis has been written by me and that to the best of my knowledge it contains no previously published material. Any help that I have received in my research work and the preparation of this thesis itself has been acknowledged. In addition, I certify that all sources of information and literature used are indicated in this thesis.

Signature of candidate



Thelma-Jean Whelan

ACKNOWLEDGMENTS

I would like to thank Professor Mick Wilson for his supervision, encouragement and support over the past three years. I would not have gotten to this point without his help. I will always be grateful for the opportunities you have given me and consider it a privilege to have worked with you.

Dr Kamali Kannangara, thank you for all your help, support and friendship. It has been a privilege working with you. To the past and present members of the research group, thank you for your friendship and encouragement.

Dr Andrew Shalliker and his research group at UWS, thank you for your friendship, support and encouragement. It has been great working with you all. Your advice and guidance over the past year and a half have been very much appreciated.

I would also like to acknowledge my supervisor Brian Reedy for his contributions to this project and to my colleagues at UTS, thanks for all your support and encouragement over the years.

To my friends, thank you for your support, encouragement and for listening to me. Your friendship is invaluable!

Most importantly I would like to thank my husband Lindsay and my Dad, Mum, Anna, Andrew and my two nieces for their love, support, encouragement and for believing in

me. They have been with me throughout the three years and I could not have completed this without them and their prayers. I am very blessed to have all of you in my life. Thank you particularly to Lindsay, who over the last months of my thesis was there with me, supporting me loving me and not letting me quit. Thank you for your patience and for believing in me. I love you!

Finally, to my Lord and saviour, the creator of everything, thank you for giving me this opportunity. All that I am and all that I do is because of you and the Grace that you have shown me.

Do you not know? Have you not heard?
The Lord in the everlasting God, the Creator of the ends of the earth.
He will not grow tired or weary and his understanding no one can fathom.
He gives strength to the weary and increases the power of the weak.
Even youths grow tired and weary and young men stumble and fall;
but those who hope in the Lord will renew their strength.
They will soar on wings like eagles; they will run and not grow weary,
they will walk and not be faint.

Isaiah 40:28-31

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Soluble organic species called humic substances are important in the Bayer process due to their adverse effect on the industrial scale production of alumina from bauxite. During the Bayer process the bauxite is subjected to a high temperature caustic digestion using sodium hydroxide. Most of the organic matter associated with the bauxite (up to 0.3%) ends up in the liquor. The soluble organic species can accumulate in the process liquor as the caustic solution is recycled for the digestion of fresh bauxite after the precipitation of the aluminium hydroxide trihydrate. In this work the humic substances were extracted from the Bayer process liquor obtained from a refinery plant operation at Kwinana Alcoa, Western Australia. The whole fraction as well as sub fractions obtained from a continuous solvent extraction were characterised by elemental and ash analysis, infrared spectroscopy, nuclear magnetic resonance spectroscopy and gas chromatography/mass spectrometry. High-performance liquid chromatography was used to further investigate the composition and structure of Bayer humic substances.

In this study a one-dimensional HPLC separation was developed for Bayer humic substances that achieved a level of separation previously unreported in the literature. The one-dimensional HPLC method separated the Bayer humic substances into compound classes. The analysis of solvent fractions allowed further assignment of the separation. Small molecules and three discrete clusters of macromolecules were observed that are believed to represent micellar like aggregates of different amounts of polar groups as supported by the results of the NMR, FTIR and GC/MS analyses. Within these clusters there was some degree of further resolution. Certain stable

configurations of molecular weights that are controlled by polarity through intramolecular binding were observed which provided strong evidence for a supramolecular structure to humic material rather than the existence of random conformational material.

To further enhance the one-dimensional separation, model compounds were studied to find the most appropriate reversed phase column for the separation of the type of compounds found in humic substances. Five new generation columns were studied with the Phenomenex Synergi polar-RP column found to offer the best performance in terms of separation. This column was later used in the development of the two-dimensional HPLC separation.

Finally, a two-dimensional reversed phase HPLC separation was successfully developed for the separation of Bayer humic substances using novel methodology developed in our laboratories, which successfully resolved uniform band profiles that showed promise of being essentially pure individual components. With the aid of mass spectrometric analysis of three second dimensional bands, the results of the separation strongly supported a host guest model for these compounds. It was concluded that small molecules are held in some way in some supramolecular structure by larger molecules (host guest complexes). The results suggested that the lower molecular weight material is capable of holding small guests more than larger molecular weight material making the supposition that the micellar host guest model is more probable than a model where hosts hide within the guests.